

EVALUATION OF MATERIALS FOR VENUS AEROBOT APPLICATIONS

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Abstract

During the last five years JPL has examined a number of concepts for robotically controlled balloons or aerobots. The Venus Geoscience Aerobot(VGA) concept uses reversible fluid altitude control to carry out repeated descents to the surface of Venus. This concept uses frozen water to keep the electronics cool. The balloon must periodically go to high altitude so that the water can be refrozen. Balloon materials would be required to withstand the rigors of the Venus atmosphere, including passes through sulfuric acid clouds and survival at temperatures up to 460°C. Polybenzoxazole(PBO) and Polyimidobenzoxazole(PIBO), materials developed by Dow Chemical Corporation, appear very promising. For example, weight loss measurements of PBO and PIBO films have been made and less than 2 percent weight loss has been observed over a four hour period at 460°C, and mechanical properties appear persistent up to high temperatures, although the high temperature limits have not been determined.

We have acquired PIBO film and tested it under conditions that simulate those encountered by a balloon in the Venus environment, including temperatures up to 500°C. It is also intended to fabricate composites made from high temperature coating/sealing material and a fabric made from PBO fibers, with PIBO as the high temperature composite matrix. A metalized PBO-based multilayer composite would be appropriate as a balloon material.

Another Venus Balloon concept, the Venus Multiprobe Mission, described in a companion paper involves higher altitude missions. While higher altitude missions have only moderate temperature requirements, balloon materials must still survive passes through sulfuric acid clouds. To meet the materials requirements for these higher altitude

missions, the focus was changed from PBO based chemistry to fluoropolymers as balloon envelope materials themselves, as a protective layer in a multilayer composite, or in a concept in which an outer "protecting" balloon is made from a fluoropolymer and the inner balloon is made from Mylar.

To evaluate fluoropolymer candidates the tensile modulus and strength of several fluoropolymers has been studied. Preliminary sulfuric acid permeation test of various fluoropolymers was performed. Sulfuric acid exposure tests were also performed on candidate fluoropolymer films as well as on fluoropolymer protected Mylar film. In these tests the mechanical properties pre and post exposure were measured and compared.

As NASA's plans for in situ exploration and sample return from Mars progress, planning is proceeding for in situ exploration and sample return from Venus. Whereas balloons and aerobots play a support role to rovers and other vehicles in the exploration of Mars, at Venus balloons play a central role for mobile exploration of the surface, acquisition of surface materials and deployment of high altitude earth return vehicles. For the Venus Surface Sample Return mission(VSSR) which does require a short 10-20 minutes Venus surface exposure (figure 1),

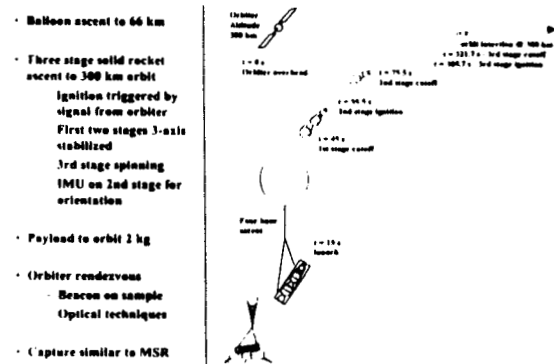


Figure 1. One Current VSSR Mission Profile

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a potentially viable balloon envelope material is PBO or carbon fiber as the reinforcing element of a fluoropolymer composite. A fluoropolymer composite has the advantage of not needing a protective metallization layer which eliminates possible problems in fabrication, storage, and deployment and inflation.

Thermogravimetric analysis of several fluoropolymers indicates very little weight loss even at temperatures as high as 460°C. Further evaluation of fluoropolymers will involve the measurement and comparison of tensile strength and modulus as a function of temperature.

Introduction

The Venusian atmospheric environment is shown schematically in Fig. 2. The surface temperature is a scorching 460°C and the pressure is more than ninety times Earth's surface pressures. The Venusian upper atmosphere between about 55 to 60 km altitude, however, has temperatures and pressures quite close to those of Earth's lower atmosphere.

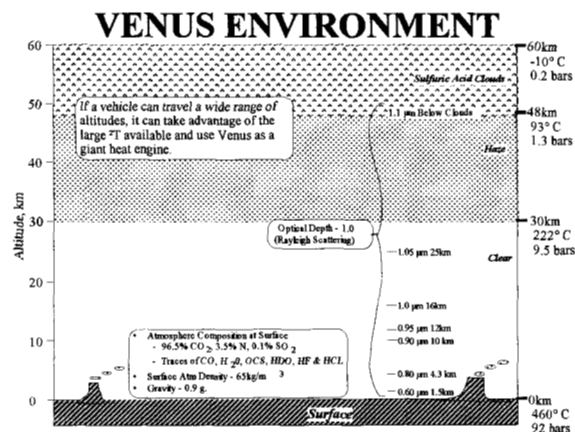


Fig. 2. Venus Environment

As a direct result of the high temperature and acidic characteristics of the Venusian atmosphere, Venus balloon envelope materials must clearly demonstrate adequate performance with respect to a number of tensile and sheering forces that such a balloon would experience. However, beyond such obvious mission requirements, a candidate material's utility as a balloon envelope designed for such indicated exploration involves numerous practical mission requirements as well. A number of Venus balloon material requirements have been discussed in a previous paper¹ in which polybenzoxazole (PBO) fiber and film were evaluated. For instance, balloon

materials must survive storage during transport through space under temperatures as low as -5°C. Furthermore, initial balloon deployment in the upper atmosphere would involve pressures of 0.5 to 3 bar coupled with temperatures of 10 to 130 C. Hence, acceptable tear performance under deployment and inflation conditions is essential.

Candidate Materials

In order to meet these rigors requirements of Venusian exploration, several candidate materials have been considered for their suitability. These materials include PBO film, PBO fiber, PIBO film, carbon fiber, PFA, PTFE, metal foils such as nickel and titanium, and various composites thereof.

The use of PBO film as the primary balloon material is attractive due to its good thermomechanical properties, that is, adequate for the support of 3 times the expected gondola load under 4 Venus mission thermal cycles, characterized between -20 to 460°C, a temperature differential corresponding to those experienced in the VGA mission as shown in Fig. 3.

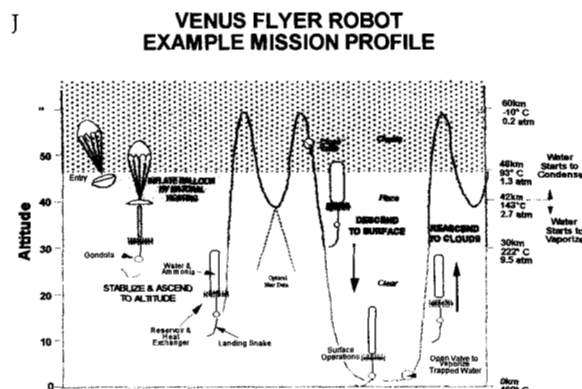


Fig. 3. Venus Geoscience Aerobot Mission

The film itself exhibits a very low degree of permeability, exceptional strength to weight ratio, promising packaging properties, and good tear resistance. However, PBO film is not an off the shelf item and, hence, the technical development required for the fabrication of a mission-ready balloon has yet to be accomplished. This development includes the large scale manufacturing of the polymer, the fabrication of the balloon from the basic polymer, metallization, sealing and seaming technologies, optical coatings, and water compatibility. Furthermore, due to PBO's incompatibility with acidic environments, coating materials, such as

noble metals, would be necessary for the protection of the high temperature polymer. Recent work by Foster Miller Inc.² indicate that protection of PBO film from conc. H₂SO₄ by gold coating appears to be difficult to achieve.

As studied in this paper, PIBO film has been shown to exhibit thermal characteristics which allow it to serve as a viable alternative to PBO as a candidate balloon material. With respect to PBO, PIBO film boasts lower RMS surface roughness values resulting from the solvent casting fabrication process. Such a process would possibly allow for easier large scale balloon fabrication as well. However, as evident in the thermal characteristics described in this paper, PIBO film is less thermally stable, not as strong, and more permeable than PBO film.

Due to the disadvantages of each of these basic materials of construction, several composite materials have been considered for their suitability with respect to Venusian balloon exploration. For instance, the use of PBO or carbon fiber in a scrim network would greatly enhance the strength of the balloon without exceeding weight limitations. A non-load bearing, seamless PIBO coating could then be applied onto the scrim to complete the balloon composite material. From such a composite design, increasing strength and better tear resistance would result. Furthermore, such composites would decrease the technological development necessary for balloon fabrication, as both PBO and carbon scrim fibers are commercially available. However, as simply a preliminary concept design, no data exists on such a composite and, hence, extensive characterization studies will undoubtedly be required.

Due to the well-documented stability of fluoropolymers towards sulfuric acid, several fluoropolymer based composites have also been proposed. Polyfluoroalkoxy (PFA) film, for instance, may be used for the protection of PBO or carbon fiber from the sulfuric acid clouds composing the Venusian atmosphere. Due to PFA's commercial availability, fabrication of such a composite may present less of a technological challenge. Moreover, resulting from PFA compatibility with both water and sulfuric acid, metalization may not be required, thereby eliminating further challenging technological development. However, with an upper temperature limit of approximately 400°C, PFA composed aerobots would not be suitable for surface excursions.

Alternatively, polytetrafluoroethylene (PTFE) has been proposed as a similar coating material to PFA, thereby increasing the thermal stability of the fluoropolymer-fiber scrim composite to as high as 430°C. Again, PBO or carbon fiber may be used for the load-bearing scrim design.

PIBO Chemistry

PIBO is an aromatic heterocyclic amorphous copolymer composed of polybenzoxazole (PBO) and polyimide moieties. Its chemical structure is shown in figure 4.

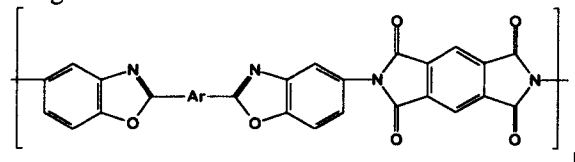


Fig. 4 Chemical Structure of PIBO

The chemical synthesis of PIBO produces a polymer which retains most of the thermal properties of PBO, but with lower or no crystallinity which results in a solvent castable polymer.

Experimental Procedures

To determine the onset of degradation of PIBO film, differential scanning calorimetric (DSC) analysis was used to measure the enthalpy change of the film with respect to temperature using a TA Instruments 2910 DSC. Thermogravimetric Analysis (TGA) was performed on the PIBO film using a TA Instruments 2950 TGA. A 38.9 mg sample was heated to 460°C to determine the degree of weight loss during high temperature exposure. The tensile thermomechanical properties of PIBO film were measured using a TA Instruments 2940 Thermomechanical Analyzer (TMA) equipped with a film and fiber assembly. The DOW Chemical Company provided the film samples which were not specifically prepared for balloon applications. Due to the solvent casting in the preparation of the film, PIBO exhibits no orientation in the tensile directions. Hence, the reported thermomechanical results are applicable in all tensile directions. The film samples were determined to have a thickness of 1.5 mil, from which thin samples approximately 0.3 mm in width were cut using a double razor blade apparatus for tensile strength measurements. Due to the force

range limitations of the thermomechanical analyzer (TMA), this thinness was necessary for the observation of force at failure. Specimens were observed under an optical microscope for accurate width measurements and evaluation for lack of uniformity and stressing occurring during sample preparation. Uniform, unstressed samples were then chosen to be clamped and mounted onto the instrument using a special mounting fixture. The sample or gage length was approximately 4 mm for all tests. The samples were then heated to temperature in approximately 3 minutes under a purge of He at 100 cc/min. During temperature equilibration, an initial weight of up to 200 grams was applied to the sample to ensure film failure within the force range limitations of the TMA. Once the desired temperature was achieved, the instrument applied an increasing force to the sample at a rate of 5 g/min until the sample broke. From this experiment, tensile strength at several temperatures up to 600°C was determined for PIBO film.

In the determination of the temperature dependence of PIBO film tensile modulus, wider samples of approximately 0.5 mm in width were used, since failure was not a concern. Similar to the tensile strength measurements, the samples were brought up to temperature in approximately 3 minutes with a constant purge of He at 100 cc/min. Unlike the tensile strength measurements however, during equilibration, no initial force was applied to the samples, and, consequently, the range of force experienced by each sample increased at 5 g/min between 0 and 100 grams. From the resulting stress/strain curves, PIBO tensile modulus was determined at several temperatures.

Measurements of the CTE of PIBO film were also made using the TMA. The film samples used were 3 mm wide and the sample or gage length was approximately 5 mm. A constant force of 5 grams was applied during temperature ramping, and dimension change was monitored and recorded. Multiple temperature cycles from room temperature to 500°C were applied with a heating rate of 10°C/min under a helium purge and the resulting dimensional changes were plotted.

Results and Discussion

Differential Scanning Calorimetric Analysis

As shown in figure 5, DSC analysis lead to the observation of film degradation temperatures of

approximately 600°C. The onset of this positive change in heat flow, occurring at approximately 420°C, can be attributed to the onset of annealing. As supported through X-Ray diffraction studies, following exposure to high temperatures, PIBO's crystallinity increases. The broad peak occurring at approximately 100°C would only correspond to the vaporization of moisture collected by the sample.

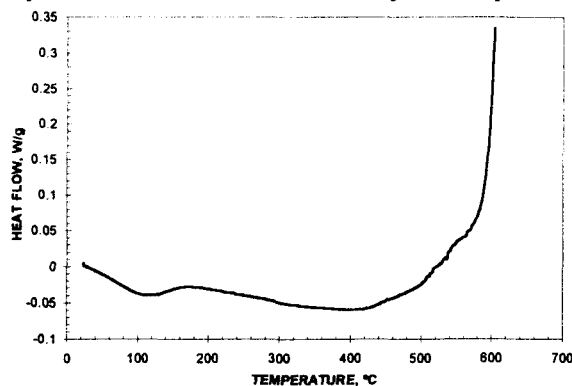


Fig. 5 Effect of Temperature on PIBO Enthalpy Change

Thermogravimetric Analysis

Following approximately 4 hours of 460°C exposure, PIBO showed good thermal stability, retaining a remarkable 98.122% of its original weight as shown in figure 6.

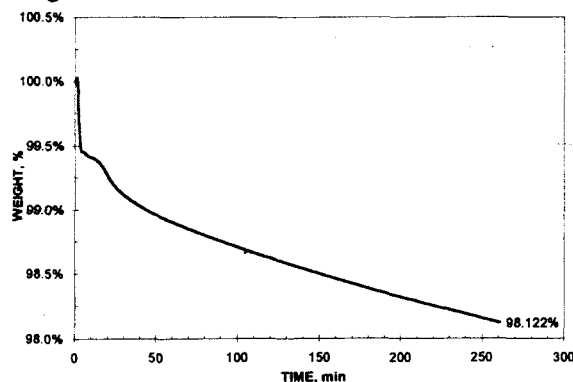


Fig. 6 Weight Loss of PIBO Film at 460°C over Time

Tensile Strength and Modulus

Figure 7 illustrates the effect of temperature on the tensile strength of PIBO measured by thermomechanical analysis. As shown, the tensile strength of PIBO decreases continuously up to 450°C followed by a steeper decrease up to 600°C. With a lower tensile strength than PBO, PIBO film will not be expected to be load bearing in the PBO/PIBO composite scrim designs. However, PIBO still

maintains good thermomechanical properties at high temperatures, demonstrated by similar tensile strength characteristics at 450°C in comparison to high performance polymers, such as Kapton and Mylar, at room temperature. In fact, PIBO at 450°C boasts better tensile strength characteristics than low-density polyethylene at room temperature, a typical material used for zero-pressure balloons.

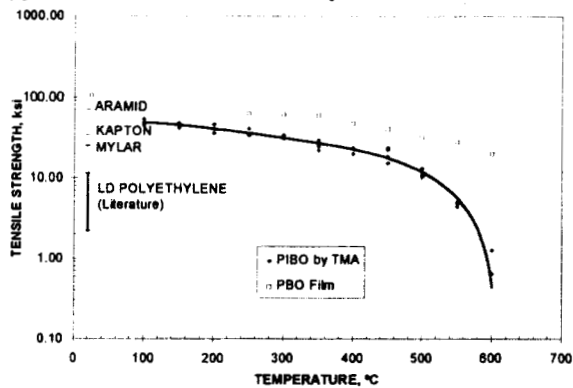


Fig. 7 The Effect of Temperature of PBO and PIBO Tensile Strength

Figure 8 illustrates the effect of temperature on the tensile modulus of PIBO with similar comparisons to PBO and low-density polyethylene. Interestingly, PIBO demonstrates an only slightly decreasing tensile modulus up to approximately 300°C, with a subsequent steeper drop up to 450°C. At these higher temperatures, above the observed glass transition temperature (T_g) of PIBO via CTE analysis, PIBO begins to flow thereby exhibiting higher modulus and elongation at failure. The ensuing rise in observed modulus at temperatures above 450°C would correspond to possible crosslinking and the onset of degradation, stiffening the material towards brittleness.

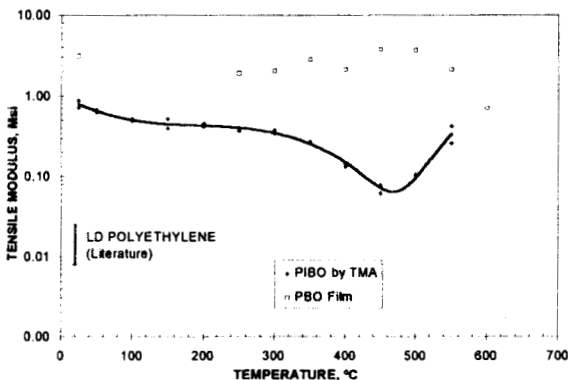


Fig. 8 The Effect of Temperature of PBO and PIBO Tensile Modulus

Therefore, at the temperature of interest, 450°C, PIBO film can be expected to have a tensile strength of approximately 20 ksi and a tensile modulus of 0.08 Msi.

CTE of PIBO Film

Figure 9 depicts PIBO film dimension change during heating. Under these conditions of temperature ramping, PIBO film exhibits a CTE of 10.0 ppm/°C up to approximately 380°C. At 390.5°C, the film begins to flow, characteristic of its glass transition temperature (T_g). Subsequent further heating induces the crosslinking and degradation of the polymer, corresponding to the sharp decline in dimension change at temperatures approaching 500°C.

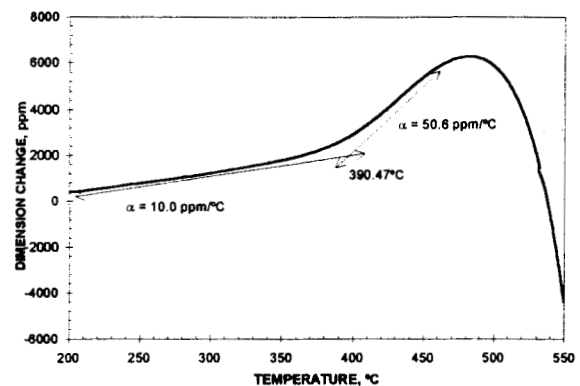


Fig. 9 CTE of PIBO Film

Under conditions of thermal cycling between room temperature and 500°C with a temperature ramp of 10°C/min, a reproducible CTE of 10.0 ppm/°C is again observed as illustrated in figure 10. Following 5 cycles of heating and cooling, an overall -9000 ppm dimension change was observed due to the onset of thermal degradation. The result is a slow shrinkage after each cycle.

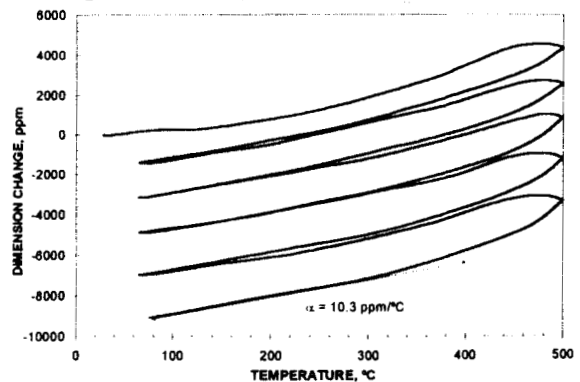


Fig. 10 Effect of Thermal Cycling on PIBO Film

This overall negative dimension change was investigated further under isothermal conditions at 460°C. As pictured in figure 11, under a constant force of 2 grams and a He purge of 150 cc/min to minimize oxidative degradation, 1.2 mm of PIBO film was temperature ramped to 460°C at 10°C/min. At this temperature PIBO film exhibited an overall linear thermal shrinkage rate of 52.46 ppm/min.

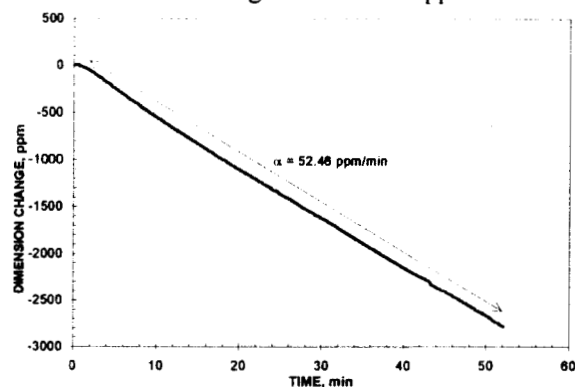


Fig. 11 Thermal Shrinkage of PIBO Film at 460°C

Mission Temperature Exposure

The PIBO film was subjected to mission temperatures of 460°C in order to test the material under Venusian conditions for a number of possible mission profiles. Samples of film were placed in glass tubes and vacuum baked overnight at 105°C to drive off excess moisture. Preliminary studies have indicated that this vacuum baking pretreatment was extremely necessary for the survival of the film following high temperature exposure. Samples not baked exhibited extremely high degrees of brittleness and degradation. Further experimentation, however, is needed to determine an optimum vacuum baking procedure. The series of sealed samples were then subjected to mission temperature exposures of increasing duration (2, 8, and 12 hours).

Figure 12 shows the effect of long term exposure to 460°C on the tensile strength of PIBO film. As depicted, PIBO exhibits a slight decrease in thermomechanical properties following exposure to mission temperatures.

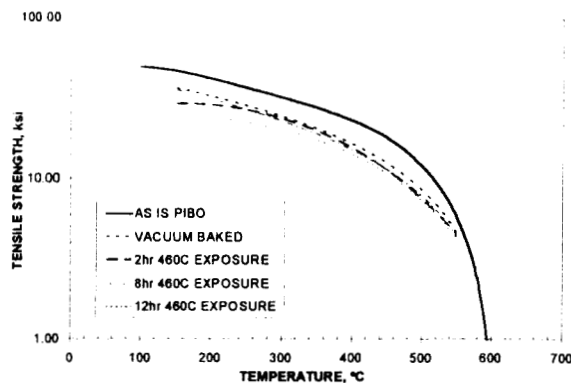


Fig. 12 Effect of Long Term Exposure to 460°C on Tensile Strength of PIBO Film

Figure 13 shows the effect of long term exposure to mission temperatures on the tensile modulus of PIBO film. Following exposure to 460°C, PIBO demonstrated an increase in tensile modulus, characteristic of the observed stiffening in the thermal exposed film. Interestingly, PIBO exhibits a significant increase in tensile modulus measured at approximately 450°C following thermal exposure. This straightening of the modulus curve would correspond to the an increase in the brittle nature of PIBO secondary to possible increased crystallinity or film degradation occurring at mission temperatures.

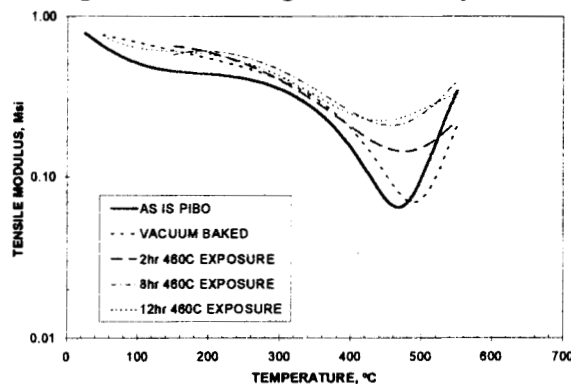


Fig. 13 Effect of Long Term Exposure to 460°C on Tensile Modulus of PIBO Film

This increasing degree of brittleness would correspond to the observed elongation at break data, illustrated in Figure 14. The lack of change in the tensile modulus in contrast to the relatively large and rapid change in elongation at film failure can be attributed to a significant decrease in the amount of PIBO film yield following exposure to high temperatures. As illustrated, even following vacuum baking at only 105°C, the elongation at break of PIBO is noticeably changed.

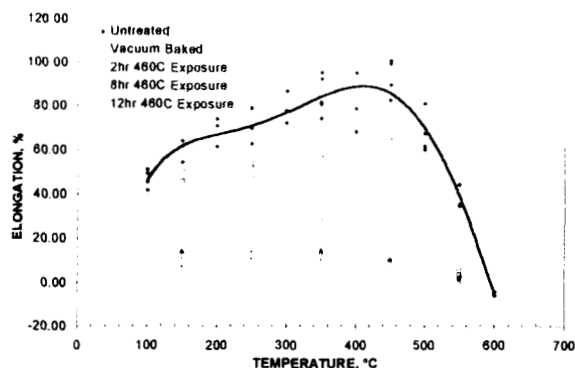


Fig. 14 Effect of Long Term Exposure to 460°C on Elongation at Break of PIBO Film

In order to investigate the possible causes of the observed stiffening in the PIBO film, correlated to the observed thermal shrinkage, X-Ray diffraction studies were performed to compare the relative crystallinities of the untreated and mission temperature exposed PIBO film samples. Following X-Ray diffraction analysis, the crystallinity of PIBO was shown to increase with exposure to 460°C mission temperatures. Therefore, such an increase in crystallinity would contribute to the observed stiffening of the PIBO film following mission temperature exposure and, furthermore, would explain the thermal shrinkage observed at temperatures above 400°C.

Consequently, the obtained data would suggest thermal cycling imparts a profound effect on the thermomechanical properties of PIBO film. However, due to the nature of this preliminary experiment, any evolved gases produced during high temperature exposure had been trapped in the sealed ampoules. These gases may have contributed to and increased the brittleness of the PIBO film and, hence, samples under vacuum or nitrogen purge should undergo further high temperature exposure testing. Nonetheless, PIBO film exhibited maintenance of thermal expansion characteristics following 460°C temperature exposures. Furthermore, the demonstration of PIBO's maintenance of tensile strength and modulus is encouraging evidence for PIBO candidacy as a Venusian balloon material, especially for the VSSR mission where the exposure to 460°C is minimal.

PBO/PIBO Composite Fabrication

In order to investigate the possibility of PIBO's use as a coating or adhesive for PBO in Venus balloon designs, several coating experiments were performed. Using a 9% solution of PIBO in 1-methyl-2-pyrrolidinone (NMP), a coating was applied to samples of PBO film and then thermally cured for polymer cyclization. The casting of the PIBO coating involved the use of shim stock to laterally border the application of the solution, thereby achieving a uniform layer of coating. The curing process, as provided by the DOW Chemical Company, involved an initial devolatilization between 80°C to 100°C. Monitoring the tackiness of the PIBO coating with a paper clip and the total coating mass, the NMP removal continued for approximately 20 minutes until the solvent concentration reached approximately 30-34%. Following the partial solvent removal, the temperature was increased to 250°C for 15 to 30 minutes. A final curing step at 400°C was implemented for 5 to 20 minutes to allow cyclization of the acid amide groups to the polyimide moieties.

To evaluate PIBO's adhesion effectiveness, a Scotch tape test was used. After affixing the tape to the PIBO coating, the tape was then removed and the PIBO adhesion to the PBO surface was observed. Following preliminary studies of coating PBO with PIBO, Scotch tape tests indicated surface treatment of PBO was required for adequate PIBO adhesion. Hence, using oxygen plasma etching (200 mtorr O₂, 125 W, 90s), the surface of PBO was pretreated prior to PIBO film casting in order to increase the strength of composite adhesion. However, further studies are necessary in order to optimize the PBO surface treatment procedure, that is to obtain the maximal PIBO surface adhesion with minimal PBO film degradation.

Following oxygen plasma etching pretreatment, PIBO was shown to have good adhesion to PBO film demonstrated by the Scotch tape test. Furthermore, following four thermal cycles from room temperature up to 460°C, the PIBO/PBO coated composite film maintained this adhesion. These tests prove the viability of a composite film made of PBO fabric impregnated or coated with PIBO.

To investigate the use of PIBO as an adhesive, two PBO samples were coated with PIBO solution. Following devolatilization, the coated samples were then joined together with pressure and allowed to cure following the same procedure. Upon observation of the final product, precipitation of the

PIBO as a yellow powder was evident, thus resulting in poor adhesion. This precipitation can be attributed to the inability of residual solvent to escape between PBO layers. To maintain PIBO coating tackiness for adhesion, however, residual solvent is necessary and therefore represents a major obstacle for the use of PIBO as an adhesive.

Thermogravimetric Analysis (TGA) was performed on the PIBO/PBO film composite to determine the degree of weight loss during high temperature exposure. Following approximately 6 hours of 460°C exposure, a 9.063 mg sample of the composite showed a retention of 96.4% of its original weight.

As an alternative to PIBO as a coating or adhesive material, preliminary experiments using DuPont "PYRALIN" PI2545 polyimide coating was performed. Following the same casting and curing procedures, a sample of both polyimide coated PBO and polyimide joined PBO was fabricated. Similar to the precipitation experiences with PIBO adhesive, the polyimide, as an adhesive, failed to form a uniform film. This precipitation, like PIBO, may be attributed to the presence of residual solvent during lamination and its inability to escape between the layers of film. However, we were successful in coating the PBO with a polyimide film and, through the Scotch tape test, polyimide was shown to have good adhesion to PBO without oxygen plasma etching pretreatment. Thermogravimetric analysis, however, exhibited a lesser degree of thermal stability with respect to the PIBO/PBO composite, illustrated by a 91.4% retention of the original 10.165 mg of composite sample following 6 hours of 460°C temperature exposure.

Fluoropolymer Evaluation

The evaluation of fluoropolymers was geared toward initial screening of the properties of interest which apply to all of the various Venus Aerobot missions as either protective coating material or as a fiber reinforced composite. In both cases the fluoropolymer is relied on as the protectant from sulfuric acid either at high temperature (surface missions) or lower temperature (higher altitude missions). preliminary testing of PTFE involved thermally degrading con. sulfuric acid on the film by heating on a hot plate at between 330 and 350°C. During the test to complete degradation of the

sulfuric acid no visible change of the PTFE film was observed. Additional preliminary testing included measurement of the permeability of sulfuric acid through PFA film. In this test con. sulfuric acid was placed on the top side of a piece of PFA film held horizontally in a glass apparatus while the under side was being constantly swept with a Nitrogen purge. The purge gas was then bubbled through a water trap. The resulting pH of the water in the trap was monitored and used to determine the permeation rate of sulfuric acid through the PFA film. The results from this test indicate a remarkably low rate of permeation. Further evaluation of the fluoropolymers was performed by TGA to test their thermal stability. Film samples of McMaster-Carr PTFE, DuPont FEP, DuPont PFA, and Chemplast PTFE were run on the TGA at 10°C/min to 600°C. As shown in figure 15, McMaster-Carr PTFE had the highest onset of degradation of >500°C.

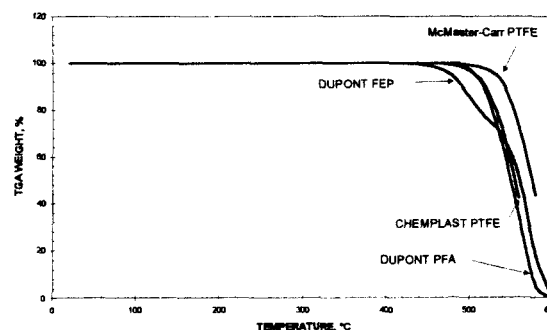


Fig. 15 Weight Loss of Fluoropolymers versus Temperature

Further TGA testing involved extended isothermal runs at temperatures approaching or equal to Venus surface mission temperatures. As shown in figure 16 McMaster-Carr PTFE film retained a remarkable 87% of its original weight after four hours at 460°C.

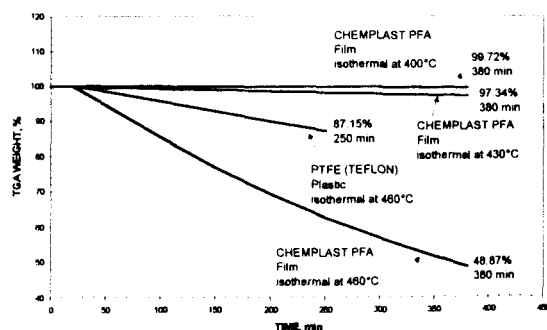


Fig. 16 Isothermal Weight Loss of Fluoropolymers

Finally, TGA analysis was performed on DuPont 150FN999 film which is a 0.5mil polyimide film coated on both sides with 0.5mil FEP. This film was heated to 125°C and dried then quickly heated to 460°C and held there for 30 minutes. As seen in figure 17 this material lost 11% of its initial weight under these extreme conditions. When heated to a slightly cooler 435°C for 30 minutes it retained a surprising 97% of its weight. This temperature is of interest for a surface mission to the tops of one of the mountainous plateaus where the increased altitude corresponds to a decrease in surface temperature.

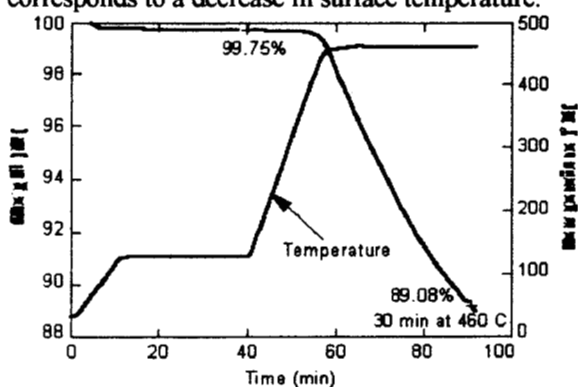


Fig. 17 FEP/Polyimide/FEP Isothermal Weight Loss at 460°C

Thermomechanical testing was performed on DuPont 150FN019 film (Polyimide/FEP) to determine how much tensile strength was retained as a function of temperature. Samples of 150FN019 were prepared following the procedure previously described. Due to the high elongation at break (80-90%) of 150FN019 as reported in the literature and observed via TMA, tensile strength could not be measured by the usual TMA methods. Hence, prior to and during the initialization of temperature, a modified procedure was utilized in stretching the film prior to the force ramp with the use of static weights or manual force. When approximately 50-70 % elongation was observed, corresponding to approximately 2000-3000 um displacement, the experimental run was rejected, and gage length was remeasured. In doing so, with the expected elongation at break at approximately 90%, film failure could be observed within the displacement limits of the TMA. Consequently, with the displacement "zeroed" at approximately 50% elongation, the run was restarted under the usual

conditions. Figure 18 summarizes those results obtained describing the thermomechanical characteristics of the DuPont 150FN019. 150FN019 shows a natural exponential decay of tensile strength with respect to temperature, thus giving a straight line in the logarithmic scale. This exponential decay of tensile strength drops from approximately 20 - 30 ksi at room temperature down to approximately 8 ksi at 500°C. The thermal tensile strength results obtained from the TMA analysis are slightly higher than those published by DuPont, however follow the same decreasing trend with higher temperatures.

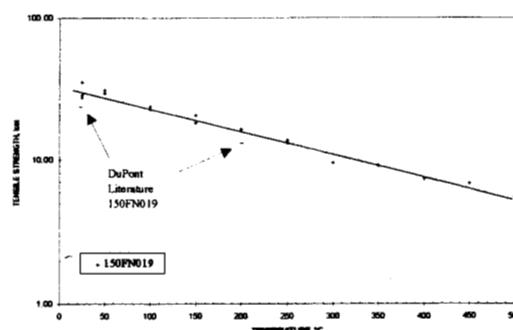


Fig. 18 Temperature Dependence of Polyimide/FEP Film Tensile Strength

In order to verify the fluoropolymers maintenance of mechanical performance following exposure to sulfuric acid, samples of each fluoropolymer (FEP, PFA, and ETFE) were immersed in solutions of concentrated and 80% sulfuric acid in small vials. As mission profiles expect 7 day sulfuric acid exposure, the samples were immersed in acid for over 10 days after which, mechanical analysis via TMA in a similar manner as previously described followed. As shown in Table 1 none of the three fluoropolymers showed a significant loss of tensile strength following exposure to sulfuric acid. However, both FEP and ETFE show a slight stiffening corresponding to a measurable increase in tensile modulus. PFA showed no change in tensile modulus following sulfuric acid exposure.

H ₂ SO ₄ Exposure:	None	10 Days 89% H ₂ SO ₄	10 Days Concentrated H ₂ SO ₄
<i>100A (HFP FEP)</i>			
Yield Strength, ksi	1.77 ± 0.05	1.74 ± 0.02	1.81 ± 0.04
Elastic Modulus, ksi	38 ± 10	66 ± 6.5	71 ± 3
<i>100LP (HFP PFA)</i>			
Yield Strength, ksi	1.74 ± 0.13	1.85 ± 0.06	1.9 ± 0.1
Elastic Modulus, ksi	61 ± 3	66 ± 1	57 ± 10
<i>150ZM (T2 ETFE) (MD)</i>			
Ultimate Tensile Strength, ksi	29 ± 4	34 ± 1	31 ± 3
Elongation at Break, %	50 ± 6	67 ± 5	67 ± 13
Yield Strength, ksi	-	-	-
Elastic Modulus, ksi	261 ± 49	286 ± 23	342 ± 20

Table 1. Effect of Sulfuric Acid on Mechanical Properties of Fluoropolymers

In order to evaluate the fluoropolymers' effectiveness in protecting any underlying material from sulfuric acid attack, samples of Mylar were covered with fluoropolymer film and then exposed to acid. Mylar was chosen for this test because it is extremely susceptible to acid and would show any effects of incomplete protection. Also Mylar, if protected from sulfuric acid would be an acceptable high altitude balloon material. Three samples of Mylar were prepared, covered with FEP, PFA, or ETFE. Taped to a 6" X 6" plate of Pyrex, the fluoropolymer covered samples of Mylar were exposed to approximately 4 drops of concentrated sulfuric acid on the side of the fluoropolymer. The acid was then sealed from air and from leakage with the use of fluorolube grease and a glass cover plate, forming an air tight barrier around the perimeter of the acid (~4" X 4"). The sample was allowed to stand for 10 days, after which, mechanical testing was performed on the Mylar via TMA. For each of the fluoropolymers used to protect the Mylar film from sulfuric acid attack, namely 1 mil FEP, 1 mil PFA, and 1.5 mil ETFE, treatment with concentrated sulfuric acid failed to reduce Mylar's observed tensile strength. Hence, the fluoropolymer's chemical compatibility with sulfuric acid provides adequate protection for Mylar against acid attack, even at thickness' of 1mil.

Conclusion

The results from these high-temperature thermomechanical tests of PIBO film on hand indicate that the material has significant retention of its tensile properties at elevated temperatures, making it a suitable candidate for short duration surface excursions as a Venus balloon envelope material or as a non-load bearing coating for Venus balloon PBO fabric/scrim composite and stitching applications.

The overall negative dimension change of PIBO during thermal cycling, resulting from thermally induced crystallinity increase, as illustrated in CTE measurements, may present some problems for the Venus balloon applications.

The Venus mission temperature exposures increased the degree of PIBO film brittleness, particularly at exposure time of greater than 8 hours.

Preliminary PIBO coating experiments show good adhesion between PIBO and PBO with oxygen plasma etching pretreatment. PIBO/PBO composite materials demonstrated good thermal stability at 460°C while thermomechanical properties have yet to be determined. Thermal cycling of the composite film did not result in delamination from CTE mismatch. However, PIBO's use as an adhesive requires further research and experimentation since preliminary tests appear to indicate PIBO cannot join PBO film.

Initial chemical compatibility results of the test involving immersion in sulfuric acid showed that the material was attacked by the acid and indicates that some protective coating will be required for Venus balloon applications.

Testing of fluoropolymers in order to evaluate their applicability as protective coatings for Venus balloon envelopes indicates that they are very suitable. They not only show extremely low permeability and susceptibility to sulfuric acid, they performed extremely well as a protective layer to sulfuric attack on Mylar.

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